Supplementary-material: Free- Electron Bound-Electron Resonant Interaction

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A. Interaction model

The interaction of a free electron with a bound electron is essentially a two-body interaction problem in the presence of a binding potential. Numerical techniques have been developed for solving similar problems in condensed matter. Our interaction model is based on adaptation of Tsubonoya's TDDFT (Time Dependent Density Functional Theory) simulation analysis of electron wave-packet scattering off a nanoflake target [1]. For a simple case where one assumes that the interaction between the free Quantum Electron Wavepacket (QEW) is electric (Coulomb interaction), the formulation is based on the TDKS (Time Dependent Kahn-Sham) equations:

$$i\hbar\frac{\partial}{\partial t}\Psi_i(\mathbf{r},t)=\left[-\frac{\hbar^2}{2}\nabla^2+\frac{1}{4\pi\varepsilon_0}\int\frac{n(r',t)}{|\mathbf{r}-\mathbf{r}'|}d^3r'+V_{ion}(\mathbf{r})+V_{xe}(\mathbf{r},t)\right]\Psi_i(\mathbf{r},t) \qquad (1)$$

Where $\Psi_i(\mathbf{r},t)$ is the wavefunction of bound electron i in the atom.

$$n(\mathbf{r}',t)=\sum_j\left|\Psi_i(\mathbf{r}',t)\right|^2+\left|\Psi^{wp}(\mathbf{r}',t)\right|^2 \qquad (2)$$

$V_{ion}(\mathbf{r})$ is the binding potential (of ion in the case of an atom), $V_{xe}(\mathbf{r},t)$ is the electrons exchange potential, and $\Psi^{wp}(\mathbf{r}',t)$ is the quantum wavefunction of the QEW.

The initial conditions are

$$n(\mathbf{r}',t)=n^{TGT}(\mathbf{r}')+\left|\Psi^{wp}(\mathbf{r}')\right|^2 \qquad (3)$$

In his model the incident electron wavepacket is represented by a Gaussian envelope wavefunction:

$$\Psi^{wp}(\mathbf{r})=\left(\frac{1}{\pi d^2}\right)^{3/4}\exp\left[-\frac{(r-b)^2}{2d^2}+ikr\right] \qquad (4)$$

where k is the de Broglie wavenumber of the electron $k=p/\hbar$.

The dynamic equation for $\Psi^{wp}(\mathbf{r},t)$ is the same as (1)

In our case, we may apply such numerical analysis for the case of a single electron atom (e.g. on Hydrogen atom or Rydberg atom), and instead of a Gaussian QEW, we would use initial conditions of an optically modulated QEW [2]. However, at this preliminary investigation of the proposed interaction effect, we resort to a simpler analytical model of a single electron QEW passing by a single two-level system (2-LS) target, interacting with the bound electron $\Psi_b(\mathbf{r},t)$ through its electric field only (magnetic field and spin effects are neglected). The electron QEW is focused in an electron microscope to a narrow cross-section relative to the impact parameter $\mathbf{r}_\perp$ (see Fig. 1a in the text) so that the exchange potential is neglected.

The equation for the bound electron is then:

$$i\hbar\frac{\partial}{\partial t}\Psi_b(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+\frac{e^2}{4\pi\varepsilon_0}\int\frac{\left|\Psi^{wp}(\mathbf{r}',t)\right|^2}{|\mathbf{r}-\mathbf{r}'|}d^3r+V_{ion}(\mathbf{r})\right]\Psi_b(\mathbf{r},t) \quad (5)$$

The equation for the free electron is

$$i\hbar\frac{\partial}{\partial t}\Psi^{wp}(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+\frac{e^2}{4\pi\varepsilon_0}\int\frac{\left|\Psi_i(\mathbf{r}',t)\right|^2}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right]\Psi^{wp}(\mathbf{r},t) \quad (6)$$

Eqs. (5,6) can be written in a generalizing way:

$$i\hbar\frac{\partial}{\partial t}\Psi_b(\mathbf{r},t)=\left[H_0+V^{wp}(\mathbf{r},t)\right]\Psi_b(\mathbf{r},t) \quad (7)$$

$$i\hbar\frac{\partial}{\partial t}\Psi^{wp}(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V^{ind}(\mathbf{r},t)\right]\Psi^{wp}(\mathbf{r},t) \quad (8)$$

Where H_0 is the Hamiltonian of the bound electron in the 2-LS target (e.g. atom), $V^{wp}(\mathbf{r})$ is the interaction potential of the bound electron with the near fields (in this case electrostatic) of the free electron, $V^{ind}(\mathbf{r})$ is the interaction potential of the free electron with the fields exerted by the target, including the field of the polarization, induced in the target by the free electron.

A general solution of the coupled equations (7,8) can be carried out iteratively where at zero order the bound electron is in the ground state of a 2-LS (or a superposition of the ground (1) and excited (2) states). The electric field experienced by the bound electron is calculated from the earlier derived expressions for the density modulation of an optically modulated QEW [2] (see next section). In the present work we solve only for the dynamics of the bound electron (Eq. 7), assuming negligible change in the wavefunction of the QEW during interaction. Solution of (8) is possible by a next iterative process in which the solution of (7) is used to derive the induced polarization field of the excited 2-LS and its effect on the free electron. This would result in a signature on the electron energy loss spectrum (EELS) of the interacting electron [3].

B. The field of a modulated QEW

As a first step of an iterative process we assume that the field $\mathbf{E}(\mathbf{r},t)$ in the interaction Hamiltonian of the bound electron $V^{wp}(\mathbf{r})$ (Eq. 7) is the near-field of the free electron modulated wavepacket at zero order approximation of Eq. (8) $\left(V^{ind}=\mathbf{0}\right)$, namely the free space propagation solution of a QEW, neglecting any recoil effect due to the induced field of the target.

A classical regime approximation for the field of the free electron, common in electron microscopy theory of EELS, is the Poisson equation solution associated with the expectation value of the classical space charge of the electron $\rho(\mathbf{r},t)=-en(\mathbf{r},z-vt)$ [4], where $n(\mathbf{r},\mathbf{t})=\left\langle\left|\Psi^{wp}(\mathbf{r},\mathbf{t})\right|^2\right\rangle$. In a disc-particle model limit of a single electron we have $n(\mathbf{r},t)=f_{e\perp}(\mathbf{r}_\perp)\delta(z-vt)$, so that $n(\mathbf{r},t)$ and $f_{e\perp}(\mathbf{r}_\perp)$ are normalized to 1. In the frequency domain

$$n(\mathbf{r},\omega)=\int_{-\infty}^{\infty}n(\mathbf{r},t)e^{i\omega t}dt=f_{e\perp}(\mathbf{r}_\perp)e^{i\omega z/v}/v \qquad (9)$$

For a narrow width current there is an analytical solution for the space charge fields of this drifting charge in the frequency domain (see Fig. 1) [3]:

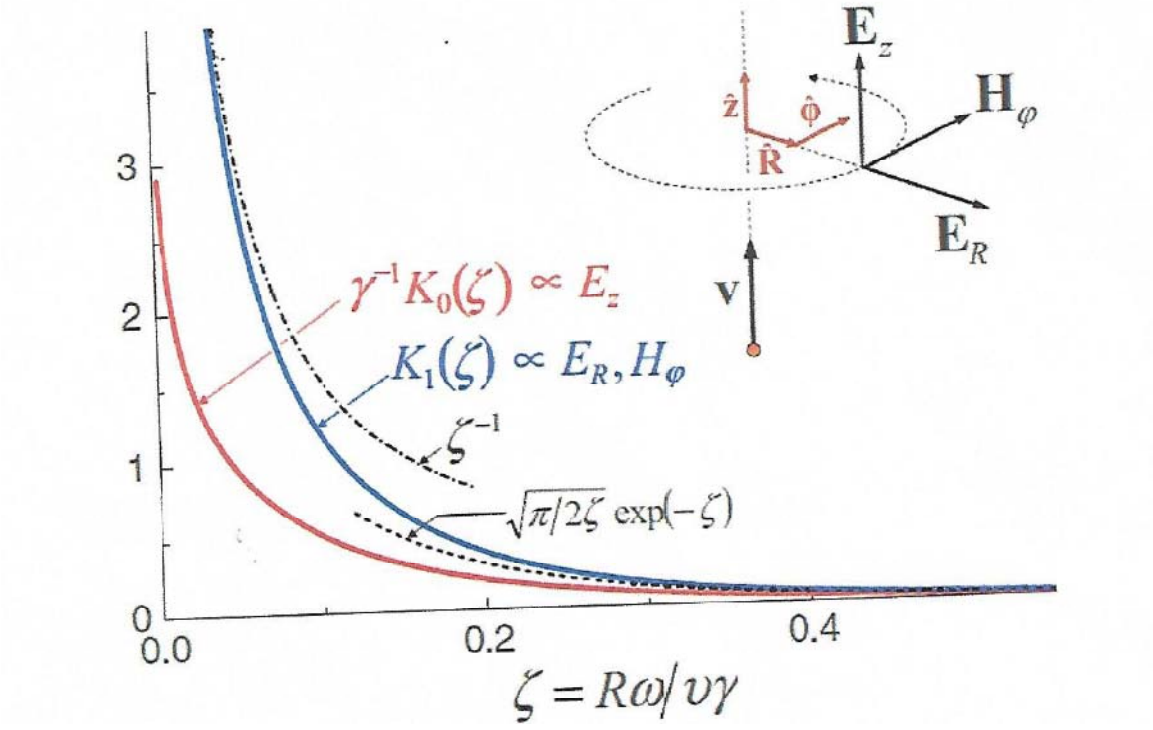

Fig. 1 *Evanescent character of the electromagnetic field produced by the exp (*$\mathrm{iw\,t}$*) of a fast electron spectral component moving in vacuum with velocity* $\mathrm{v} = 0.7\mathrm{c}$ $(\mathrm{y} \approx 1.4$ *and kinetic energy* $\approx 200\mathrm{keV})$ *along the positive z axis. The only non-vanishing components* $\left(\mathrm{E_R}, \mathrm{E_z} \text{ and } \mathrm{H_j}\right)$ *decay exponentially at large distance R from the trajectory. The inset shows the orientation of these components relative to the electron velocity vector. (From [3])*

$$\mathbf{E}(\mathbf{r},\omega) = \int_{-\infty}^{\infty} \mathbf{E}(\mathbf{r},\mathrm{t})\, \mathrm{e}^{\mathrm{i}\omega\mathrm{t}}\mathrm{dt} = \frac{1}{2\pi\epsilon_0}\frac{\mathrm{e}\omega}{\mathrm{v}^2\gamma_\epsilon\epsilon_\mathrm{r}}\mathbf{g}(\mathbf{r}_\perp)\,\mathrm{e}^{\mathrm{i}\omega\mathrm{z}/\mathrm{v}} \qquad (10)$$

$$\mathbf{g}(\mathbf{r}_\perp) = \left[\frac{1}{\gamma_\epsilon}\mathrm{K}_0\left(\frac{\omega\mathrm{r}_\perp}{\mathrm{v}\gamma_\epsilon}\right)\hat{\mathbf{z}} - \mathrm{K}_1\left(\frac{\omega\mathrm{r}_\perp}{\mathrm{v}\gamma_\epsilon}\right)\hat{\mathbf{r}}_\perp\right] \qquad (11)$$

$$\mathbf{H}(\mathbf{r},\omega) = \frac{1}{2\pi\epsilon_0}\frac{\mathrm{e}\omega}{\mathrm{vc}\gamma_\epsilon}\mathrm{K}_1\left(\frac{\omega\mathrm{r}_\perp}{\mathrm{v}\gamma_\epsilon}\right)\mathrm{e}^{\mathrm{i}\omega\mathrm{z}/\mathrm{v}}\hat{\boldsymbol{\varphi}} \qquad (12)$$

where $\gamma_\epsilon = 1/\sqrt{1-\epsilon_\mathrm{r}\beta^2}$, $\epsilon_\mathrm{r} = \epsilon/\epsilon_0$ $\beta = \mathrm{v}/\mathrm{c}$ $\mathbf{r} = (\mathbf{r}_\perp, \mathrm{z})$, $\mathbf{r}_\perp = (\mathrm{x}, \mathrm{y})$.

In the present analysis we use the same approximation to evaluate the field associated with optical frequency density bunching of a quantum electron wavepacket (QEW). Such modulation takes place when the QEW is energy-modulated in the near field of a laser-illuminated nanostructure [2] or a foil [9], or by the pondermotive field of the beat of two laser beams [10], and then allowed to drift for some distance after interaction, which converts the energy modulation to density modulation [2, 10, 11]. The density $\mathrm{n}(\mathbf{r},\mathrm{t}) = \left\langle\left|\Psi(\mathbf{r},\mathrm{t})\right|^2\right\rangle$ of the modulated QEW can be written as a

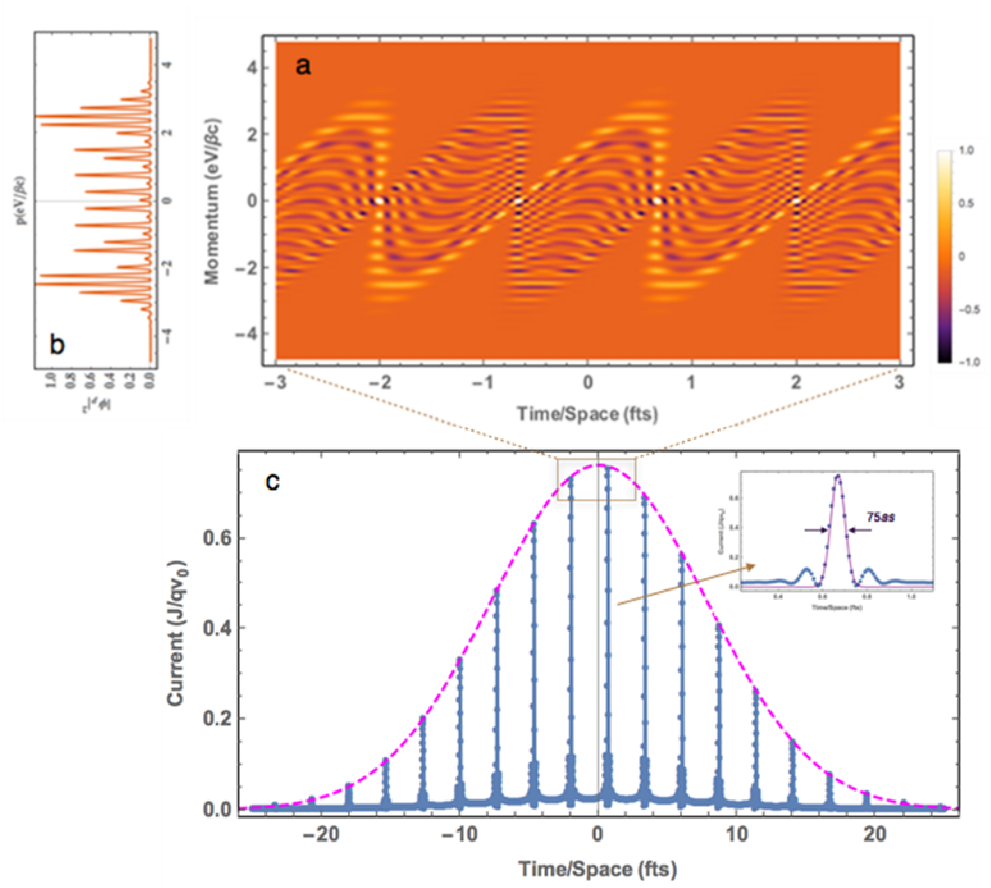

Fig.*2. The momentum/ - space/time phase-space (Wigner) distribution of an electron quantum Wavepacket after energy modulation in the near field of a tip illuminated by a laser and subsequent drift in free space. b. Multi-sidebands momentum distribution. c. Tight periodic bunching spatial/temporal distribution of the optical frequency of the modulating laser beam taken from Feist [2]).*

sum of harmonics of the modulation frequency ω_b within the envelope of the QEW [4]:

$$n(\mathbf{r},t)=\frac{1}{v_0}f_{e\perp}(\mathbf{r}_\perp)f_{et}(t-t_0-z/v)f_{mod}(t-z/v_0) \tag{13}$$

$$f_{mod}(t)=\sum_{n=-\infty}^{\infty}B_n e^{-in\omega_b t} \tag{14}$$

where the envelope function is normalized in time: $\int f_e(t)\,dt=1$.

The density modulation is a consequence of the nonlinear energy-momentum dispersion relation of an electron in free-space propagation. The "PINEM sidebands" components of the single electron modulated QEW [2] spaced $\hbar\omega_b$ apart, propagate at

different "chirped" phase, and their interference after drift time t_D creates the density modulation of the QEW $n(\mathbf{r},t)=\left\langle\left|\Psi(\mathbf{r},t)\right|^2\right\rangle$. Maximum modulation takes place at [4]

$$t_{D,max}=\frac{1}{2}\frac{T_b}{\Delta p_m/p_0} \qquad (15)$$

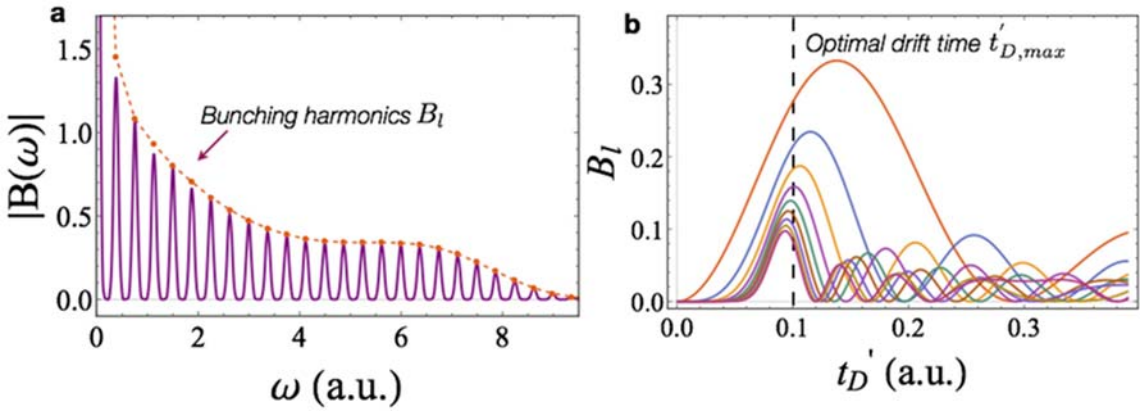

Fig. 3 *The frequency spectrum of the density modulation function. b. The bunching amplitudes of the harmonic frequencies as a function of drift time.*

where $T_b=2\pi/\omega_b$ and $\Delta p_m/p_0$ is the momentum modulation coefficient. Fig. 2c depicts the density modulation of the QEW as a function of time, calculated for the parameters of Feist [2]. Fig. 3 shows the corresponding bunching spectrum of the density modulation function (3a) and the bunching coefficients of the different harmonics at the maximum modulation point $t_{D,max}$ (15), all calculated for a model of a normalized Gaussian envelope of the QEW

$$f_{e,t}(t)=\left(\sqrt{2\pi}\sigma_{et}\right)^{-1}e^{-t^2/2\sigma_{et}^2}. \qquad (16)$$

The Fourier transform of the density modulated QEW (4) is:

$$n(\mathbf{r},\omega)=\frac{1}{v}f_\perp(\mathbf{r}_\perp)e^{i\omega z/v}\sum_n B_n e^{i(\omega-n\omega_b)t_0}F_e(\omega-n\omega_b) \qquad (17)$$

where $F_e(\omega)=\mathcal{F}\{f_{et}(t)\}=\int_{-\infty}^{\infty}f_{et}(t)e^{i\omega t}dt$. For the normalized Gaussian (16):

$F_e(\omega)=e^{-\sigma_t^2\omega^2/2}$, and the spectral width of the harmonic is $\Delta\omega=\pi/\sigma_{et}$.

The spatial dependence of (17) is the same as (9), and therefore, for a narrow QEW, we have the same solution (9-12) of Maxwell equations for the fields with the corresponding harmonic frequency dependent coefficients:

$$\mathbf{E}(\mathbf{r},\omega)=\sum_{n=-\infty}^{\infty}E_n(\mathbf{r},\omega)$$

$$\mathbf{E}_n(\mathbf{r},\omega) \approx \frac{1}{2\pi\epsilon_0}\frac{e\omega_n}{v^2\gamma_\epsilon\epsilon_r} B_n \mathbf{g}_n(\mathbf{r}_\perp) e^{i(\omega-\omega_n)t_0} F_e(\omega-\omega_n) e^{i\omega z/v} \qquad (18)$$

$$\mathbf{g}_n(\mathbf{r}_\perp) = \frac{1}{\gamma_\epsilon} K_0\left(\frac{\omega_n r_\perp}{v\gamma_\epsilon}\right)\hat{\mathbf{z}} - K_1\left(\frac{\omega_n r_\perp}{v\gamma_\epsilon}\right)\hat{\mathbf{r}}_\perp \qquad (19),$$

and we set in (19) $\omega = \omega_n$ under the assumption that the spectral linewidth function $F_e(\omega-\omega_n)$ is narrow enough when the modulation period is small relative to the QEW length σ_t. The field spectrum is composed then of multiple harmonics $\omega_n = n\omega_b \ (n \neq 0)$, all of spectral width $2\pi/\sigma_t$. These fields decay within an interaction range $r_{\perp,int} = \beta\gamma\lambda_n/2\pi$ in the range $r_\perp \rangle \sigma_\perp$ under the approximation of a narrow beam $\sigma_\perp$.

Inverse Fourier transforming (18) back to the space-time domain one obtains

$$\mathbf{E}(\mathbf{r},t) = \frac{1}{2\pi\epsilon_0}\frac{e}{v^2\gamma_\epsilon\epsilon_r} f_{et}(t-t_0-z/v)\sum_n \omega_n B_n \mathbf{g}_n(\mathbf{r}) e^{i\omega_n(t-z/v)} \qquad (20)$$

$$\mathbf{g}_n(\mathbf{r}_\perp) = \left[\frac{1}{\gamma_\epsilon} K_0\left(\frac{\omega_n r_\perp}{v\gamma_\epsilon}\right)\hat{\mathbf{z}} - K_1\left(\frac{\omega_n r_\perp}{v\gamma_\epsilon}\right)\hat{\mathbf{r}}_\perp\right] \qquad (21)$$

This result could also be derived directly in time domain by solution of Maxwell equations with charge $en(\mathbf{r},t)$ given by Eqs. 13, 14.

We can write (20, 21) as

$$\mathbf{E}(\mathbf{r},t) = f_e(t-t_0-z/v)\sum_n \boldsymbol{\mathcal{E}}_{0n}(\mathbf{r}_\perp) e^{i\omega_n(t-z/v)} \qquad (22)$$

$$\boldsymbol{\mathcal{E}}_{0n}(\mathbf{r}_\perp) = \frac{1}{2\pi\epsilon_0}\frac{e\omega_n}{v^2\gamma_\epsilon\epsilon_r} B_n \mathbf{g}_n(r_\perp) \qquad (23)$$

C. <u>Electric dipole quantum transitions of a two-level system</u>

Neglecting any spin and magnetic interactions, let us approximate the Coulomb interaction potential in (5) or (7) by an electric dipole interaction Hamiltonian:

$$V^{wp} = -e\mathbf{E}(t)\cdot\mathbf{r} \qquad (24)$$

where $\mathbf{E}(\mathbf{r},t)$ is the electric field created by the density modulated QEW at the location of the 2-LS target:

$$E(t) = E_0 \cos(\omega_0 t - \varphi_0) = \frac{1}{2} E_0 e^{i(\omega_0 t - \varphi_0)} + \text{c.c.}$$

We solve the 2-LS excitation problem similarly to the way it is solved for coherent laser interaction with an atom [5, 6, 15]:

$$\Psi_b(\mathbf{r}, t) = a_1(t)\varphi_1(\mathbf{r}) e^{-iE_1 t/\hbar} + a_2(t)\varphi_2(\mathbf{r}) e^{-iE_2 t/\hbar} \qquad (25)$$

Where $\varphi_1(\mathbf{r})$, $\varphi_2(\mathbf{r})$ are the eigenfunctions of the non-interacting 2-LS. Substituting in (7) results in

$$i\hbar\left[a_1'(t) e^{-iE_1 t/\hbar}\varphi_1(\mathbf{r}) + a_2'(t) e^{-iE_2 t/\hbar}\varphi_2(\mathbf{r})\right] = V(\mathbf{r}, t)\left[a_1(t) e^{-iE_1 t/\hbar}\varphi_1(\mathbf{r}) + a_2(t) e^{-iE_2 t/\hbar}\varphi_2(\mathbf{r})\right]$$

Multiplying by $\varphi_1^*(\mathbf{r})$, $\varphi_2^*(\mathbf{r})$ and integrating, using the orthogonality of the eigenfunctions, we get

$$a_1'(t) = -\frac{i}{\hbar}\left[V_{11} a_1(t) + V_{12} e^{-i\omega_{21} t} a_2(t)\right] \qquad (26)$$

$$a_2'(t) = -\frac{i}{\hbar}\left[V_{21} a_1(t) e^{i\omega_{21} t} + V_{22} a_2(t)\right] \qquad (27)$$

$$\omega_{21} = (E_2 - E_1)/\hbar \qquad (28)$$

Where $V_{ij} = \int \varphi_i^*(\mathbf{r}) V(\mathbf{r}) \varphi_j(\mathbf{r}) d^3 r$.

Assume $V_{11} = 0 \quad V_{22} = 0 \quad V_{21} = V_{12}^*$ and $V_{12} = A(t) e^{i\omega_0 t}$, then:

$$a_1'(t) = -\frac{i}{\hbar} A(t) e^{i\Delta\omega t} a_2(t) \qquad (29)$$

$$a_2'(t) = -\frac{i}{\hbar} A^*(t) e^{-i\Delta\omega t} a_1(t) \qquad (30)$$

$$\Delta\omega = \omega_0 - \omega_{21} \qquad (31)$$

Assume now the simplest case of resonant interaction $\Delta\omega = 0$ and $A(t) = \text{const}$. This can be achieved by controlling the frequency of the laser:

$$a_1'(t) = -\frac{i}{\hbar} A a_2(t)$$

$$a_2'(t) = -\frac{i}{\hbar} A^* a_1(t)$$

$$a_1''(t) = \frac{-\Omega_R^2}{4} a_1(t) \qquad (32)$$

$$\Omega_R = 2|A|/\hbar = 2|V_{12}|/\hbar = \boldsymbol{\mu}_{12} \cdot \mathbf{E_0}/\hbar \qquad (33)$$

With initial conditions $a_1(0) = 1 \quad a_2(0) = 0$:

$$a_2(t) = -i \sin \frac{\Omega_R}{2} t \qquad (34)$$

$$a_1(t) = \cos \frac{\Omega_R}{2} t \qquad (35)$$

where $\mathbf{E}(t) = (\mathbf{E}_0/2) e^{i\omega_0 t - i\varphi_0}$, μ_{12} - the dipole moment of the 2-LS transition.

The probability of occupying the upper level after time t is:

$$P_2(t) = |a_2(t)|^2 = \sin^2 \frac{\Omega_R}{2} t \,. \qquad (36)$$

D. An ensemble of correlated quantum electron wavepackets

Consider now an ensemble (pulse) of N QEWs, all modulated by the same coherent laser beam and thus having phase correlation, and propagating along the same axis [4] (see Fig. 1c in the text). The QEWs may enter at random time t_{0j}. Considering one of the harmonics n of Eq. 20, the resultant field of the N_e electrons in the pulse is

$$\mathbf{E}_n^{pulse}(\omega, \mathbf{r}) = \mathbf{E}_{0n} F_e(\omega - \omega_n) e^{i\omega_n z/v} \sum_{j=1}^{N_e} e^{i(\omega-\omega_n)t_{0j}} \qquad (37)$$

where for a Gaussian QEW (16): $F(\omega) = e^{-\sigma_{et}^2 \omega^2/2}$.

We define a pulse bunching coefficient:

$$b_n^{pulse} = \frac{1}{N_e} \sum_{j=1}^{N_e} e^{i(\omega - n\omega_b)t_{0j}} \qquad (38)$$

Assume that the electron pulse statistical temporal distribution is $f_p(t_{0j})$, such that $\int_{-\infty}^{\infty} f_p(t_{0j})\, dt_{oj} = 1$. Following [4], for $N_e \rangle\rangle 1$ we can replace the summation of (38) by integration:

$$\left\langle b_n^{pulse} \right\rangle = F_p(\omega - \omega_n) = \int f(t_{0j}) e^{i(\omega-\omega_n)t_{0j}} dt_{0j} \qquad (39)$$

(For example, if $f\left(t_{0j}\right)=\frac{1}{\sqrt{2\pi}\sigma_p}e^{-t_{0j}^2/2\sigma_p^2}$ then

$$F_p\left(\omega\right)=e^{-\sigma_p^2\omega^2/2} \qquad (40)$$

Since the pulse duration is much longer than the QEW - $\sigma_p \rangle\rangle \sigma_{et}$, the envelope frequency spectral width $\Delta\omega_{pulse} \sim 2\pi/\sigma_p$ is much narrower than the width of the QEW envelope spectral width $\Delta\omega_\ell = 2\pi/\sigma_{et}$, and therefore we may set in (37)

$F_e\left(\omega-\omega_n\right) \sim F_e\left(0\right)=\int_{-\infty}^{\infty} f_{et}\left(t\right)dt=1$, and

$$\bar{\mathbf{E}}_n^{pulse}\left(\omega,\mathbf{r}\right)=N\mathbf{E}_{0n}F_p\left(\omega-\omega_n\right)e^{i\omega_n z/v} \qquad (41)$$

Back Fourier transformation produces

$$\bar{\mathbf{E}}_n^{pulse}\left(\mathbf{r},t\right)=N\mathbf{E}_{0n}f_p\left(t-z/v\right)e^{i\omega_n\left(t-z/v\right)} \qquad (42)$$

which signifies that the harmonic field of the pulse of modulated QEWs is equivalent in intensity to $N_e\sigma_{et}/\sigma_p$ times the field of a single modulated QEW, and its duration is σ_p/σ_{et} times longer.

E. Simulation of excitation of a two-level system by a train of phase correlated pulses

As is evident from the previous section, the near field of an ensemble of QEWs, tightly bunched at optical frequency and phase correlated (in their modulation phase), contains a substantial coherent component of harmonic frequencies of the modulation frequency. It may then interact with a 2-LS system in a manner equivalent to that of a long uninform continuous pulse, as in Section C. To verify this assumption, we simulate the interaction of an ensemble of quantum electron wavefunctions with the 2-LS system by solving the set of coupled equations 29, 30 for a potential made of a sum of N_e potentials of the near fields of the QEWs, modeled as identical size and amplitude rect(t/T_e) functions:

$$V^{pulse}=\boldsymbol{\mu}_{12}\cdot\mathbf{E}_0e^{i\omega_n t+\varphi_j}\sum_{j=1}^{N_e}\mathrm{rect}\left(\frac{t-t_{0j}-T_e/2}{T_e}\right) \qquad (43)$$

We integrate Eqs. 29, 30 piece-wise by using the trivial solution (34, 35) for each uniform segment, but setting the initial condition for each step to be given by the amplitude and phase of the previous interaction step:

$$\begin{aligned} a_2(t_{0j})&=a_2(t_{0j-1}+T_e)\\ a_1(t_{0j})&=a_1(t_{0j-1}+T_e)\end{aligned} \qquad (44)$$

Fig. 2a in the text displays the probability of excitation of level 2 - $P_2(t)=\left|a_2(t)\right|^2$ as a function of time for an ensemble of phase correlated pulses ($\varphi_j=0$ for all j) and random t_{0j} for the case of exact resonance $\Delta\omega=0$. This multiple interaction events curve is compared to the case of a single uniform pulse (blue curve) (Eq. 36), with good match. For comparison, simulation

parameters are normalized to accumulate on the average the same Rabi phase $\Phi_R(t) = \int_0^t \mu_{12}\bar{E}_0(t')dt'/\hbar$. In this model the comparison basis is for the average electric field $\bar{E}_0 = E_0 N_e T_e / T_p$, namely the effective field for the coherent buildup of Rabi oscillation is weighed by the ratio between the integrated duration of the micro-pulses and the duration of the pulse, but the accumulated Rabi phase of the multiple random envelope correlated-phase interaction grows in proportion to N_e : $\Phi_R^{pulse} = \bar{\Omega}_R T_p = N_e \Phi_R$. Fig. 2b in the text shows the build-up of the occupation probability of level 2 in the case of uncorrelated QEWs, namely – their phases φ_{0j} are random. Evidently the growth is slower, and does not arrive to full occupation. The blue curve is an average over several simulation events, confirming the initial linear buildup of the upper level population as a function of N_e in the absence of relaxation.

F. Free-Electron Bound-Electron Resonant Interaction (FEBERI)

In Ref. 4 we conjectured that the coherent part of the spectrum of a train of density-modulation phase-correlated QEW would give rise to coherent superradiant and stimulated superradiant emission when interacting with radiation field (e.g. in Smith-Purcell radiation. Here we make a conjecture that this coherent part of the spectrum can interact resonantly with matter, and specifically, with a 2-LS target.

We consider two cases of excitation of the upper level of a 2-LS target by a pulse of N_e phase correlated QEWs (Fig. 1c in the text). First we derive the condition for fully coherent excitation of the upper quantum level via a π pulse of Rabi oscillation with N_π correlated QEWs. Secondly, we derive the probability of exciting the upper level with $N_e \langle N_\pi$. We presume that the excitation level can be monitored by measurement of the cathodoluminescence (CL) intensity at resonance and out of resonance and in the absence of modulation.

We refer to the field of a single harmonic n of N_e QEWs, that is the inverse Fourier transform of (41), N_e time the harmonic field component of a single modulated QEW (22,23).

$$\bar{\mathcal{E}}_n^{pulse} = N_e \mathcal{E}_{0n} f_p\left(t - z/v\right) e^{i\omega_n (t - z/v)} \qquad (45)$$

Take a case of uniform distribution of particles in the pulse:

$$f_p(t) = \frac{1}{T_p}\,\mathrm{rect}\left(\frac{t}{T_p}\right) \qquad (46)$$

so that $\int f_p(t)\,dt = 1$. Using (23), the maximal field amplitude to be used in (33) for the Rabi frequency is:

$$E_{0n}^{N_e} = \frac{N_e \mathcal{E}_{0n}}{T_p} = \frac{1}{2\pi\epsilon_0}\frac{e\omega_n}{v^2\gamma_\epsilon\epsilon_r}\mathbf{g}_n(r_\perp)\frac{N_e}{T_p} \qquad (47)$$

The Rabi phase is then:

$$\Phi_{Rn}^{N_e} = N_e f_{Rn}$$

$$f_{Rn} = \Omega_R T_p = \frac{\mathbf{m}_{12} \cdot \mathbf{E}_0}{\hbar} T_p \qquad (48)$$

Substituting this in (48) and setting $\mathbf{m}_{12} = e\mathbf{r}_{12}$, it can be written as:

$$\Phi_{Rn}^{N_e} = \frac{1}{2\pi\epsilon_0} \frac{e^2 w_n}{c^2 \hbar} \left(\frac{\mathbf{r}_{12} \cdot \mathbf{g}_n(\mathbf{r}_\perp)}{b^2 g^2 \epsilon_r} \right) N_e = \qquad (49)$$

$$= 4\pi\alpha \left(\frac{\mathbf{r}_{12} \cdot \mathbf{g}_n(\mathbf{r}_\perp)}{\lambda_n b^2 g^2 \epsilon_r} \right) N_e$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137}$, $\lambda_n = 2\pi c / w_n$.

For complete transfer of population to the upper level (π-pulse) it is required that $\Phi_R = \pi$.

For a crude estimate of the number of correlated QEWs required for such a π-pulse transition, we take $r_{12} \sim 1\text{nm}$, $\lambda_\ell \approx 0.2\mu\text{m}$ $\left(g_\ell(r_\perp) / b^2 g^2 \epsilon_r \right) \sim 1$

$$\Phi_R = \frac{4\pi}{137} \cdot 5 \times 10^{-3} N \approx 0.15\pi \times 10^{-3} N = \pi$$

$$\longrightarrow N_p = 7 \times 10^3$$

This corresponds to a charge of about 1 femtoCoulomb that is within the state of the art of photocathode emission, but space-charge effects within the beam would prohibit tight focusing of the beam on the target. If attainment of coherent Rabi Oscillation may be difficult to realize, we can still consider the rate of resonant excitation of a 2-LS targets by a pulse of modulated QEWs on the basis of probability of excitation of a single 2-LS.

For the case $\Phi_R(t) = \Omega_R t \langle\langle \pi$ one can expand (34, 36) to first order, and then the probability for exciting level 2 after interaction with a pulse of duration time $t = t_p$ is:

$$P_2(T_p) = \frac{1}{4} \Phi_R^2(T_p) = \frac{1}{4} \Omega_R^2 T_p^2 \qquad (50)$$

If the pulses of m-QEWs are phase correlated (which may be possible with state of the art mode-locked laser technology), and the pulse rep. rate of the modulating laser is fast relative to the relaxation time of the excited level 2, the coherent Rabi oscillation process may persist. In the opposite case, it would be interrupted. The case of a randomly interrupted 2-LS should be treated separately. If the system does not relax between pulses the solutions (34) and consequently (50) should be modified, and solved

after each dephasing relaxation event with proper different randomly renewed initial conditions, leading to a random-walk statistical build-up of the population of level 2.

For the case of multiple interaction events with a 2-LS target or multiple number of excited 2-LS targets with $P_2 \langle\langle 1$, we may define an average excitation rate per single 2-LS target:

$$W_i = \frac{P\left(T_p\right)}{T_p} = \frac{1}{4}\Omega_R^2 T_p \qquad (51)$$

E. Experimental considerations

The new concepts of FEBERI and RCL with single QEWs and with an ensemble of correlated QEWs, were presented here in the framework of a simplified model. Further technological developments are required for realizing these concepts in the lab and in new applications of electron microscopy. Here we make some crude estimates on the the viability of these concepts, referring to real parameters of a material target of interest, such as NV defect centers in diamond. We first check how many phase-correlated modulated QEWs would be required to produce a full π-phase Rabi transition and satisfy Eq. 14. In diamond NV centers there is a 2-LS quantum transition of $\Delta E = 1.945 eV$ [7], and it thus can be excited resonantly by the second harmonic field component of a pulse of QEWs, modulated by an infrared laser of $\lambda_b = 1.27 \mu m$. With a rough estimate $\left(g_n(r_\perp)B_n / \beta^2 \gamma_\varepsilon \varepsilon_r\right) \approx 1$, one obtains $N_\pi = 2.2 x 10^4$, which corresponds to 3.7 femtoCoulomb. This may be excessive charge for the femtosecond laser driven photoemission techniques used in PINEM [12, 13], and one may be concerned about energy spread and loss of modulation coherence due to Coulomb interaction scattering in the electron pulse [14]. However, since the relaxation time of the 2-LS can be in a much longer time scale (t_r=13.5 nSec for Diamond N-V center [7]), one may resort to operating with longer electron pulse generation and laser modulation techniques [13], and mitigate the Coulomb scattering problem. Alternatively, if one operates in the weak coupling regime with a smaller number of correlated modulated QEWs (say, $N_e = 10^2 \langle\langle N_\pi$ generated by a 10GHs mode locked laser within 10nSec), one can still attain an enhancement factor of RCL by a factor N_e relative to the conventional CL from the same number of electrons.

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